Chinese Chemical Letters Vol. 14, No. 11, pp 1141 – 1143, 2003 1141
http://www.imm.ac.cn/journal/ccl.html

Two New Diterpenoids from *Hedychium forrestii*

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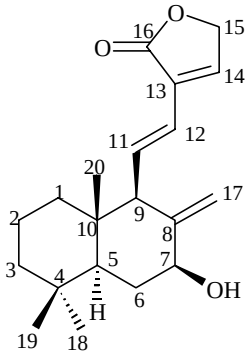
Abstract: Two new labdane diterpenes isolated from the rhizomes of *Hedychium forrestii* were determined by spectroscopic evidence to be labda-8(17), 11, 13-trien-7 β -hydroxyl-15(16)-olide (**1**, hedyforrestin B) and labda-8(17), 11, 13-trien-7 β ,16-dihydroxyl-16(15)-olide (**2,** hedyforrestin C).

Keywords: *Hedychium forrestii*, diterpene, hedyforrestin B and C.

Previous studies on the genus *Hedychium* resulted in obtaining some labdane-type diterpenoids which showed significant cytotoxic activities against V-79 and KB cells[1~3]. Recently, we studied the chemical constituents of *H. forrestii* in the continuation of this research, and two new labdane-type diterpenoids were obtained.

Hedyforrestin B (**1**), needles (from petroleum-ethyl acetate), $[\alpha]_D^{23}$ = + 14.30 (*c* 0.402, $CHCl_3$), HREIMS established its molecular formula to be $C_{20}H_{28}O_3$ (316.2029, calcd 316.2038). The IR spectrum gave an absorption band due to α,β-unsaturated



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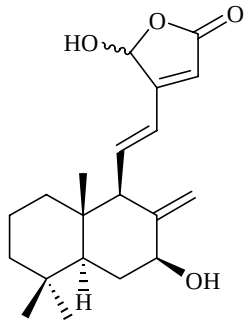

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γ-lactone (1752 cm^{-1}), and hydroxyl group (3350 cm^{-1}). The ^1H NMR spectra indicated the presence of three methyl groups (δ_H 0.85, 0.87, 0.92) and an *exo*-methylene (δ_H 4.72, 5.14), which were characteristic of labdane-type diterpenoids, and confirmed by the characteristic EIMS fragment ion peak at *m/z* 137. The ^{13}C NMR spectra (DEPT) gave

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20 carbon signals, including one carbonyl carbon (δ_C 172.24). In the ^{1}H NMR spectra, signals for two *trans* olefinic proton signals were observed at δ_H 6.12 (d, J = 16.0 Hz) and δ_H 6.92 (dd, J = 10.5, 16.0 Hz), respectively. The latter one was downfield shifted because the *trans* olefinic group was linked directly to the α , β -unsaturated γ-lactone[1] . The comparison of ^{1}H and ^{13}C NMR spectra of **1** with those of coronarin A[1] showed that the difference was the six-carbon moiety at C-9 (namely, C11~16 moiety). The ^{1}H and ^{13}C NMR assignments were determined from ^{1}H-^{1}H COSY, HMQC and HMBC. The ^{1}H-^{13}C long-range correlation between H-12 (δ_H 6.12) and the carbonyl carbon (δ_C 172.24) indicated that this functional group was located at C-16 rather than at C-15. The α-axial orientation of H-9 and H-5 was elucidated by the cross-peak between H-9 and H-5 in ROESY. Therefore, the side chain at C-9 was determined to be β-form. Furthermore, the α-axial orientation of H-7 was confirmed by the cross-peaks between H-7 and H-9, and between H-7 and H-5 in ROESY, which indicated the hydroxyl group at C-7 to be β-form. Therefore, the structure of **1** was elucidated to be labda-8(17), 11, 13-trien-7β-hydroxyl-15(16)-olide.

Table 1 The ^{1}H NMR(500MHz) and ^{13}C NMR(125MHz) data for **1** and **2** ($CDCl_3$, δ, ppm)

C	**1**		**2**	
	δ_C	δ_H	δ_C	δ_H
1	40.33		40.51,40.38	
2	18.99		18.98	
3	41.91		41.86	
4	33.44		33.44	
5	52.51	1.16 dd(1.5, 12.5)	52.49	1.14 br.d(12.1)
6	33.15		32.93	
7	73.22	4.08 dd(5.5, 11.0)	73.12	4.07 dd(5.4, 11.0)
8	151.26		150.53,150.25	
9	60.38	2.32 d(10.5)	60.34	2.38 d(10.0)
10	39.26		39.53,39.64	
11	135.44	6.92 dd(10.5, 16.0)	142.36	6.57 dd(10.0, 15.9); 6.56 dd(10.1, 15.9)
12	121.01	6.12 d(16.0)	123.08	6.33 d(15.9); 6.34 d(15.9)
13	129.34		161.47	
14	142.87	7.18 s	115.77	5.85 s, 5.84s
15	69.59	4.82 s	171.77	
16	172.24		98.04	6.26 s; 6.28 s
17a	105.22	4.72 s	106.07,105.68	4.67 s; 4.58s
17b		5.14 s		5.14 s; 5.12s
18	33.49	0.85 s	33.50	0.84s
19	21.81	0.87 s	21.85	0.85s
20	14.99	0.92 s	15.13	0.91s

Coupling constants(Hz) in parentheses.

Hedyforrestin C (**2**) was obtained as colorless oil, $[\alpha]_D^{23}$ = +21.37 (*c* 0.386, $CHCl_3$). HREIMS established its molecular formula to be $C_{20}H_{28}O_4$ (332.1983, calcd 332.1988).

The IR spectrum gave an absorption band due to an α,β-unsaturated γ-lactone (1734 cm^{-1}), and hydroxyl group(3392 cm^{-1}). The comparison of ^{1}H and ^{13}C NMR spectra (DEPT) of **2** with those of **1** indicated the same skeleton for both **2** and **1** (**Table 1**), the difference was the structure of α,β-unsaturated γ-lactone at C-12. The ^{13}C NMR signals of **2** assigned to C-1, C-8, C-10 and C-17 appeared in pairs, indicating that **2** was a mixture of two epimers at C-16 hydroxyl group which could not be chromatographically separated from each other. Furthermore, The ^{1}H NMR signals of **2** assigned to H-11 and H-12 seemed to be complicated, and H-14, H-16, H-17a, and H-17b appeared in pairs. The only difference between **2** and yunnancoronarin[3] C was the hydroxyl substitution at C-7 in the former and at C-6 in the latter. The NMR assignments for **2** were carried out on the basis of ^{1}H-^{1}H COSY, HMQC and HMBC. The HMBC showed the ^{1}H-^{13}C long-range correlation between H-12 (δ 6.33 and 6.34) and the hemi-acetal carbon (δ 98.04), indicating that the hemi-acetal group was located at C-16, and the carbonyl group at C-15. The three cross peaks between H-9 and H-7, H-9 and H-5, H-7 and H-5 in ROESY suggested the α-axial orientation of H-9, H-7 and H-5. Thus the side chain at C-9 was determined to be β-form, and the C-7 hydroxyl group was β-form. Therefore, the structure of **2** was determined to be labda-8(17),11,13-trien-7 β ,16-dihydroxyl-16(15) -olide. Similar to the known coumpound yunnancoronarin[3] C, the C-16 hydroxyl group in **2** was ether α- or β-orientated..

Acknowledgment

Program granted by the Laboratory of Phytochemstry, Kunming Institute of Botany, the Chinese Academy of Sciences

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Received 29 September, 2003